

# UNCLASSIFIED

AD NUMBER
AD831119
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational use; Mar 1968. Other requests shall be referred to Air Force Materials Lab, Wright-Patterson, AFB OH.
AUTHORITY
USAF ltr 12 Jan 1972

THIS PAGE IS UNCLASSIFIED

AD831119

AFML-TR-67-235

## LITERATURE SURVEY ON THE EFFECTS OF LONG-TERM SHELF AGING ON ELASTOMERIC MATERIALS

CARMEN L. BELLANCA  
JAY C. HARRIS

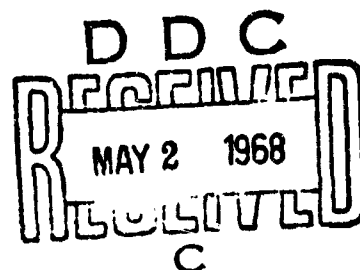
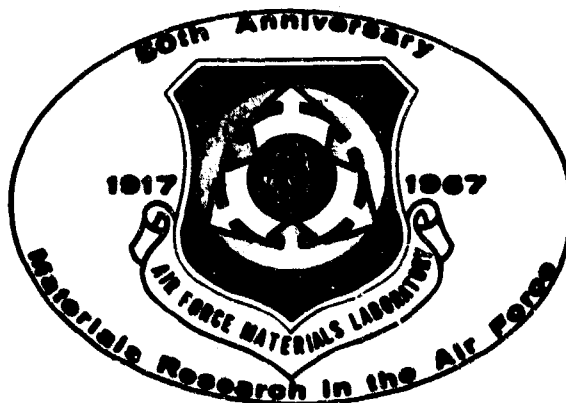
MONSANTO RESEARCH CORPORATION

TECHNICAL REPORT AFML-TR-67-235

MARCH 1968

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAAE), Wright-Patterson Air Force Base, Ohio 45433.

AIR FORCE MATERIALS LABORATORY  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433



# NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

ACG Section 121	
CFSTI	WHITE SECTION <input type="checkbox"/>
DOC	DIFF SECTION <input checked="" type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
DIST.	AVAIL. and/or SPECIAL
2	

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

## FOREWORD

This report was prepared by Monsanto Research Corporation, Dayton Laboratory, under Air Force Contract No. AF 33(615)-1484, and was initiated under Project 7381, "Materials Applications," Task 738102, "Materials and Processes Evaluation."

The work was administered under the direction of the Materials Applications Division, Air Force Materials Laboratory, Directorate of Laboratories, Wright-Patterson Air Force Base, Ohio, with Mr. Phillip A. House as project engineer.

This report covers work performed from November 1965 to November 1966, at the Dayton Laboratory of Monsanto Research Corporation, and was submitted August 1967 for publication.

The survey was performed by Carmen L. Bellanca with Jay C. Harris serving as project Manager.

This technical report has been reviewed and is approved.

*Albert Olevitch*

Albert Olevitch, Chief  
Materials Engineering Branch  
Materials Application Division  
Air Force Materials Laboratory

### ABSTRACT

Literature was surveyed with regard to the effects of long-term storage on the properties of elastomeric compounds. Data showed that most elastomeric compounds aged well. Elongation at break appeared to be the property most commonly affected by age deterioration, although compression set and change in strain also are affected.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAAE), Wright-Patterson Air Force Base, Ohio 45433.

# **LITERATURE SURVEY ON THE EFFECTS OF LONG-TERM SHELF AGING ON ELASTOMERIC MATERIALS**

**CARMEN L. BELLANCA**

**JAY C. HARRIS**

**This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAAE), Wright-Patterson Air Force Base, Ohio 45433.**

## TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
I	INTRODUCTION	1
II	SUMMARY AND CONCLUSIONS	2
III	RECOMMENDATIONS	3
IV	DISCUSSION	4
	A. Rubber Manufacturers' Association	6
	B. O-Ring Manufacturer's Data	11
	C. Mare Island Naval Shipyard Rubber Laboratory	11
	D. Pensacola Naval Air Station - Materials Engineering Division	11
	E. Precision Rubber Products	11
	F. Rock Island Arsenal	12
	G. Oklahoma City Air Material Area (OCAMA)	12
	H. Mobile Air Material Area	13
	I. Compression Set Aging Study - OCAMA	14
	J. Society of Automotive Engineers (SAE)	14
	APPENDIX	15
	Figures 1 - 5	
	Tables I - XXIX	
	REFERENCES	

## LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Neoprene: Effect of Aging on Elongation at Break ( $E_B$ ).	16
2	Nitrile: Effect of Aging on Elongation at Break ( $E_B$ ).	17
3	Effect of Aging at Various Temperatures on Ultimate Elongation.	18
4	Percent Change in Strain with Time After Aging Indoors.	19
5	Percent Change in Strain with Time After Aging Outdoors.	20



LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Physical Properties of Vulcanizates Aged Indoors Ten Years (Percent Change from Original Values)	21
II	Physical Properties of Vulcanizates Aged Outdoors Ten Years (Percent Change from Original Values)	22
III	Strain Data for Heat Aged Vulcanizates	23
IV	Strain Data for Indoor Aged Vulcanizates	24
V	Strain Data for Outdoor Aged Vulcanizates	24
VI	Physical Property Change of Commercial Nitrile Compounds - RMA	25
VII	Physical Property Change of Commercial Neoprene Compounds - RMA	25
VIII	Physical Property Change of Butyl Rubber Compounds - RMA	26
IX	Physical Property Change - MIL-P-5516, Class B - RMA	26
X	Physical Property Change - MIL-G-5510A and MIL-P-5315A Compounds - RMA	27
XI	Physical Property Change - MIL-P-25732 and MIL-P-18017 Compounds - RMA	27
XII	Physical Property Change of Overage O-Rings - Manufacturer's Data	28
XIII	Physical Property Change of Overage O-Rings - Manufacturer's Data	29
XIV	Effect of Shelf Aging on MIL-P-5516 O-Rings - Mare Island Naval Shipyard	30
XV	Physical Properties of Aged Vulcanizates - Precision Rubber	31

# LIST OF TABLES (Cont'd)

<u>Table</u>		<u>Page</u>
XVI	The Effect of Shelf Storage Life on the Physical Properties of Silicone, Fluorosilicone, and Fluorocarbon Vulcanizates	32
XVII	O-Ring Physical Properties After Storage - OCAMA - MIL-P-5516 - Manufacturer A	33
XVIII	O-Ring Physical Properties After Storage - OCAMA - MIL-P-5516 - Manufacturer B	34
XIX	O-Ring Physical Properties After Storage - OCAMA - MIL-P-5516 - Manufacturer C	35
XX	O-Ring Physical Properties After Storage - OCAMA - MIL-P-5516 - Manufacturer D	36
XXI	O-Ring Physical Properties After Storage - OCAMA - MIL-P-5315 - Manufacturer A	37
XXII	O-Ring Physical Properties After Storage - OCAMA - MIL-P-5315 - Manufacturer B	38
XXIII	O-Ring Physical Properties After Storage - Mobile - MIL-P-5516 - Manufacturer A	39
XXIV	O-Ring Physical Properties After Storage - Mobile - MIL-P-5516 - Manufacturer B	40
XXV	O-Ring Physical Properties After Storage - Mobile - AMS-7270	41
XXVI	O-Ring Physical Properties After Storage - Mobile - AMS-7271	42
XXVII	O-Ring Physical Properties After Storage - Mobile - AMS-7274	43
XXVIII	O-Ring Physical Properties After Storage - Mobile - MIL-P-5315 - Manufacturer A	44
XXIX	Stored O-Ring Physical Property Change After Oven Aging - Monsanto - MIL-R-7362 O-Rings	45

## SECTION I

### INTRODUCTION

There presently exist military standards which are intended as guides for use by storage activities involved in the supply of rubber products. Generally, these standards have established maximum time periods for the shelf storage life of rubber products. The shelf storage life refers to the maximum period of time from cure date, during which the item is expected to retain its ability to function as originally specified. Since maximum storage periods are recommended, rubber goods are either disposed of at the end of the storage periods or updated by the testing of certain physical properties and determining whether the rubber is still useful.

As long-term storage data which define the effect of shelf storage of long periods on elastomeric physical properties are generated, it is becoming more apparent that the life expectancy of specification rubber items when stored under normal military conditions is somewhat longer than heretofore believed. The data point out that reconsideration of age control over these items may be in order.

Consequently, this literature survey was conducted with regard to the effect of long storage times (i.e., 10 years) on the physical properties of molded rubber products corresponding to various military specifications. Additional literature which was felt to be of value in elucidating the aging properties of elastomers was surveyed. This survey describing elastomeric aging is by no means a complete one since the literature in this area is voluminous; consequently, the only literature studied was that considered most directly pertinent.

## SECTION II

### SUMMARY AND CONCLUSIONS

Literature was surveyed with regard to the effects of long-term storage on the properties of elastomeric compounds. The survey was undertaken to determine whether present age control restrictions on military specification elastomeric materials should be reconsidered.

Long-term storage data pointed out that, in general, elastomeric compounds which met military specifications aged well under normal military storage conditions. Most compounds showed fairly good retention of the original physical properties after storage periods as long as ten years.

The property showing the greatest change after prolonged storage periods was tensile modulus. This was not surprising, since the elongation of most elastomers tested tended to decrease while the ultimate tensile strength either increased from the original or showed little change.

Great changes in modulus levels did not appear to define realistically the extent of degradation. Elongation at break appeared to be the parameter most commonly affected by aging. Other parameters affected were compression set and change in strain at constant load with time.

### SECTION III

#### RECOMMENDATIONS

Based on long-term storage data from tests conducted by Air Force Air Material areas and by the Rubber Manufacturers' Association, it is recommended:

- (1) that the matter of age control restrictions on stored rubber items be reconsidered. The data show that storage limitations on many specification materials can be loosened to increase maximum storage times.
- (2) that the properties after high temperature aging of stored elastomers be further evaluated. Data by Mobile AMA indicate that stored MIL-R-7362 Buna N would meet original physical property requirements, but requirements after aging at 275°F could not be met. Tests by Monsanto Research Corporation supported the Mobile data.
- (3) that consideration be given to new standards of judging the suitability of stored specification materials rather than just the determination of physical property changes upon shelf aging. Commonly reported shelf aging data indicate changes in stress-strain, hardness, and modulus. However, it is becoming increasingly evident that these parameters do not fully characterize age deterioration. Testing of properties such as compression set, strain, and stress relaxation would appear to indicate more readily small changes in materials due to aging.
- (4) that long-term aging tests be conducted on silicone and fluorocarbon elastomer compounds. Very little long-term storage data are available for these high performance materials, and increasing usage of them warrants background information on their long-term stability.

## SECTION IV

### DISCUSSION

Shelf aging of elastomers is a slow process which generally takes place over a number of years. However, it often is desirable to be able to predict the life and/or the degree of deterioration of elastomeric articles after a storage period. Since it is difficult, if not impractical, to obtain the necessary physical property degradation data from long-term aging studies (e.g., 10 years) prior to use, accelerated aging tests have been designed. These such as oven aging, oxygen and ozone exposure, and fluid immersion are well-known throughout the rubber industry.

An overall change in physical properties generally results from accelerated aging tests. Changes can be misleading at times because the relationship between the degree of change and the extent of degradation is inconclusive. Tensile, modulus, and hardness can either increase or decrease upon oven aging of elastomers, whereas elongation only decreases.

Ultimate elongation appeared to be the most representative property to express the deterioration of elastomeric compounds with age. Mandel, et al. (1), made a mathematical study of aging data reported in the literature. The following equation was developed from this work and expresses the elongation at break after room temperature aging:

$$E = E_0 - kt^{0.5} \quad (1)$$

where E is the elongation at break after aging for time t,  $E_0$  is the extrapolated elongation at time zero, and k is a velocity constant.

Utilizing this equation, Stokoe (2) attempted to estimate the service life of nitrile and neoprene compounds under various conditions. Experimental data obtained for elongation at break were plotted according to the above equation; the plots are given in Figures 1 and 2. As shown, the points approximate a straight line. If we assume 100 percent elongation at break to be the criterion of failure, then the life of the neoprene compounds is approximately 16 years outdoors and 30 years indoors. The nitrile compounds would be serviceable for 25 years indoors and 12 years outdoors. This predicted life assumes no unusual factors.

Cosgarea, et al. (3), aged nitrile O-rings at 25°, 50°, 65°, 80°, and 100°C from 2 to 240 days. The ultimate elongation data were correlated as a function of time according to Mandel's equation in an attempt to predict aging properties. Results obtained at 100°C were discarded due to the possibility of a different aging reaction mechanism at this high temperature. From the data reduction, the predicted time for a 20% reduction in elongation ranged from 2.25 to 2.75 years at 25°C; the predicted time to reach an ultimate elongation of 150% ranged from 6.50 to 7.33 years.

The equation developed by Mandel, et al., expresses the early part of the aging process, e.g., room temperature aging up to 10 years. However, the prediction of shelf aging from tests at two or more elevated temperatures is possible only if the relationship between aging and temperature is known.

Mandel, et al. (1), treated the parameter  $k$  as a reaction rate constant, assuming the decrease in ultimate elongation upon aging to be the result of a single chemical reaction. If this is true, then according to the Arrhenius equation,

$$\ln k = \frac{-\Delta H}{RT} + C \quad (2)$$

a plot of  $\ln k$  versus  $1/T$  should be linear. This was indeed the case as shown in Figure 3. As noted, the curves appear to be linear. However, as the test temperature increased, the rate of aging increased much faster than predicted.

Bergstrom (4) aged vulcanizates of styrene-butadiene (SBR), neoprene, butadiene-acrylonitrile (NBR), and butyl indoors and outdoors for 10 years under unstressed conditions. Air oven aging tests were conducted at 158°F concurrently to determine if any correlation existed between accelerated and natural (indoor and outdoor) aging.

Figures 4 and 5 show the change in strain over the 10-year aging period. Tables I and II summarize the changes in tensile, elongation, hardness, and strain at 200 psi load. It is seen that the butyl vulcanizate aged less over the 10-year period than any of the other vulcanizates. This was probably due to the lower degree of unsaturation in the butyl chain compared to the other test polymers. Aging degradation is generally associated with unsaturation; i.e., the less the unsaturation, the less the degradation. Further, it was shown that the vulcanizates aged more outdoors than indoors. However, from these data, all of the compounds tested could be considered useful after 5 years of aging, depending upon the application.

Specimens of representative vulcanizates were aged at 158°F from 1 to 419 days. Percent retention of strain data are given in Table III; these data are compared to indoor and outdoor data shown in Tables IV and V. It is noted that aging vulcanizates for periods up to as much as 20 days at 158°F did not have the expected deleterious effect on strain properties. It appeared that oven aging at 158°F was not a severe enough accelerated test for indoor-aged SBR, neoprene, and NBR vulcanizates as indicated by the data of Tables IV and V.

In other work, Bergstrom (5) attempted to correlate natural aging with accelerated aging at 212°F of SBR, natural rubber, and NBR compounds. The vulcanizates were aged indoors and outdoors up to six years. Air oven aging tests were conducted at 212°F for periods from 70 hours to 14 days. It was found that the relative resistance to deterioration of different types of elastomers could be predicted reasonably well from the accelerated aging tests. However, no direct correlation existed between oven and natural aging for a particular elastomer. The resistance to age degradation of a particular elastomer varies according to the ingredients it contains, i.e., antioxidants, antiozonants, acceleration system, plasticizer type, etc. As a consequence, it became apparent that to attempt to predict the effect of natural aging solely on accelerated aging data would be futile.

A number of programs were undertaken to determine (1) the effect of long-term shelf aging on elastomer physical properties, and (2) serviceability after long periods of storage and field service. Summaries of these programs follow. In selecting representative data for the condensed tables, it was difficult if not impossible to follow one single compound or composition throughout. Either the data were insufficiently identified, or data points, selected by those reporting the data, which skipped periods not leading to a clear-cut follow through. The objective in any event was to select representative values and to cite extremes rather than presenting every data value given in original reports.

#### A. RUBBER MANUFACTURERS' ASSOCIATION

The Rubber Manufacturers' Association (R.M.A.), O-Ring Division, studied the degradation of tensile, elongation, modulus, and hardness properties of O-rings of a variety of compounds submitted by several member companies (6). The intent of the program was to test for periods of 10 to 20 years.

The materials tested include commercial nitrile, commercial neoprene, butyl rubber, and compounds which meet specification MIL-P-5516. Some of the participating members have submitted



additional types of materials. These include compounds conforming to military specifications MIL-G-5510, MIL-P-5315, MIL-P-18017, and MIL-P-25732. All of the specification materials are nitrile rubbers. Representative data are shown in Tables VI-XI.

1. Effect of Aging on Commercial Nitrile Compounds (Table VI)

a. Modulus at 100% Elongation

Aging of several commercial nitrile compounds showed that the modulus at 100% elongation changed the most of the physical properties evaluated. It might be suspected that extremes of modulus could occur at periods of exposure less than the maximum. That this was the case was true for one compound which after 2 years exposure showed a 53% increase. Other compounds after 6 years exposure varied from +15% to 49% with values as low as 8% after 5 years. The data of Table VI represents the values for three more typical compounds selected from a total of 17, up to a maximum of 7 years exposure.

b. Elongation

According to data reported for 17 compounds, the elongation at break generally decreased with time. After 6 years of aging, the maximum elongation change was -27%. In some cases, the change in elongation was as low as -4% after 6 years. In general, after the initial change in elongation (1 to 1.5 years), any subsequent change was usually of the same magnitude. There did not appear to be gross changes in elongation over the 7-year period.

c. Tensile Strength

After 7 years aging of 17 compounds, the maximum change in tensile strength was +21%. In one case, change in ultimate tensile strength after 7 years was +1.0%. Tensile strength of the tested compounds was generally level through 4 years of aging. Further, the greatest change usually occurred in the first year or two and then leveled off.

d. Hardness

Hardness data were obtained from 11 compounds and showed an average change of +5 points after 7 years. The maximum change noted was +10 points. The hardness of the compounds tended to increase slowly with time, although this was not unexpected.

Generally, the nitrile compounds under test showed no gross degradation after 7 years of storage. However, the extent of degradation is relative because it is dependent upon the limits set in material specifications and the specific application. For example, a particular item covered by a specification allowing only a five-point increase in hardness might show a ten-point increase after 7 years of storage, and could possibly still be considered usable.

## 2. Effect of Aging on Commercial Neoprene Compounds (Table VII)

### a. Modulus at 100% Elongation

As in the case of the nitrile compounds, modulus at 100% elongation of the neoprene compounds evaluated showed the greatest change. Five compounds were tested. One showed an increase in modulus of 125% after 7.75 years. Other of the five compounds not included in the table ranged from 33% to 111%. Large increases (24% to 56%) were noted after only 1.25 years of storage. A steady increase was noted thereafter.

### b. Elongation

The ultimate elongation loss for all of the five compounds averaged approximately 35% after 7.75 years of storage. The elongation decrease during the first year of storage and thereafter remained essentially constant.

### c. Tensile Strength

Generally, the ultimate tensile strength of the compounds evaluated did not show much change through 7.75 years of storage. Change in tensile strength in most cases appeared to reach a maximum at approximately 2 years and to level off thereafter. One compound showed a tensile strength decrease of 22.7% after 7.75 years; at 2 years it had decreased 14%.

### d. Hardness

All of the neoprene compounds increased in hardness to approximately the same degree (8-10 points) after storage for 7.75 years. The increase in hardness appeared to remain constant for the last 4 to 5 years after increasing rather rapidly early in the storage period.

### 3. Effect of Aging on Commercial Butyl Compounds (Table VIII)

#### a. Modulus at 100% Elongation

Limited data from four compounds are available from the R.M.A. study which characterized the change in modulus of butyl with time. The limited study showed that one compound had an increase of 87% in modulus after 5.75 years of storage, another +9.2% after 4 years, and another +12% after only 1.75 years of storage. These data pointed out the wide variation in age resistance possible within specific elastomer classes through compounding techniques.

#### b. Elongation

The changes in ultimate elongation varied widely, e.g., -6% to -28% at 5.75 years, -20% at 1.75 years. This again pointed out the variation in properties obtainable from a single elastomer through compounding techniques.

#### c. Tensile Strength

The ultimate tensile strength of butyl compounds stored 7.75 years increased approximately 12% to 16%. None of the compounds tested show excessive changes through the test period.

#### d. Hardness

The change in hardness of the butyl compounds showed no set pattern and was probably dependent on compounding techniques. For example, after 7.75 years of storage, one compound increased 10 points in hardness, while another lost 1 point. Only limited data were available on other compounds, but they indicated slight change, i.e., +1 after 4 years, +1 after 1.75 years.

### 4. MIL-P-5516, Class B Compounds (Table IX)

#### a. Modulus at 100% Elongation

Modulus data were reported from four compounds meeting the above specification. The data showed that wide variations in modulus were obtained even though all compounds were directed toward the same specification. One compound showed over 85% increase in modulus after 6.75 years of storage, while a second, not shown, increased 24% in 7.25 years.

b. Elongation

The compounds showed fairly good retention of ultimate elongation through 4.75 years of storage (-14.4% max.) and increased to a maximum of -23.7% after 5.75 years. All O-rings still had at least 150% elongation, which should be sufficient for most applications.

c. Tensile Strength

None of the O-rings tested showed great changes in tensile strength after 6.75 years of storage. The maximum change noted was +22% (not shown) after 4.25 years; the minimum was -0.20% after 7.25 years, also not shown.

d. Hardness

No great changes in hardness were noted after 7.75 years of storage at room temperature. The maximum change was +14 points (not shown) after 7.5 years. A change to this extent may be considered excessive for specific O-ring applications (i.e., loaded O-rings).

5. MIL-G-5510A and MIL-P-5315A Compounds (Table X)

Since only three compounds were tested, limited data were available on these compounds. None of the tests showed great changes in tensile strength or hardness after 7.5 years of storage. One compound showed an appreciable decrease in ultimate elongation (-41%); whether the O-rings are serviceable would depend on the specific application. Very limited data showed an increase in modulus through 7.5 years storage of 34% and another, not shown, of +68.1% after 7.75 years.

6. MIL-P-25732 and MIL-P-18017 Compounds (Table XI)

Very limited long-term storage data were available on these compounds; two compounds representative of MIL-P-25732 and one for MIL-P-18017 were tested. Only one had been stored as long as 7.5 years. Data showed an appreciable increase in hardness (+15 points) after 7.5 years, but relatively small changes in ultimate tensile and elongation (+19% and -23%, respectively). The small changes in properties imply that the O-rings are still serviceable.

#### B. O-RING MANUFACTURER'S DATA

In 1963, some Buna N O-ring manufacturers conducted tests of average samples of their O-rings returned by Mobile Air Materiel Area. These represented Specifications MIL-P-5516, MIL-P-5315, AMS-7274, and AMS-7270. The O-rings were 5 to 7.5 years old.

The test results indicated that all the O-rings evaluated were considered still serviceable. Representative data are shown in Tables XII and XIII. The most appreciable change was found in ultimate elongation, but the particular O-rings maintained sufficient elongation for usage. No large changes in hardness or tensile strength were observed, and many showed small decreases in ultimate elongation.

#### C. MARE ISLAND NAVAL SHIPYARD RUBBER LABORATORY

The Rubber Laboratory of Mare Island Naval Shipyard investigated the effect of long-term shelf aging on O-rings conforming to Specification MIL-P-5516 (7). Data are shown in Table XIV. O-Rings which had reached the maximum allowable storage age of 4 years were tested after an additional 4 years of shelf aging. No significant changes in physical properties were observed after 8 years. It was concluded from these tests that the O-rings will give satisfactory service after at least 8 years of shelf aging.

#### D. PENSACOLA NAVAL AIR STATION - MATERIALS ENGINEERING DIVISION

The Materials Engineering Division of Pensacola Naval Air Station evaluated O-rings conforming to MIL-P-5315 (8) to determine the change in physical properties after extended storage and to determine whether age resistance was affected by extended storage. O-Rings aged 1 to 7 years were tested. Original physical properties, and properties after aging 70 hours and 168 hours at 212°F were recorded. No serious degradation in original properties or reduction in age resistance were found to result when O-rings were stored up to 5 years.

#### E. PRECISION RUBBER PRODUCTS

Precision Rubber Products Corporation, Dayton, Ohio, reported an in-house program (9) in which compounds of several elastomers have undergone shelf aging tests. Data obtained from neoprene and nitrile compounds were included in the R.M.A. program and will not be discussed here. However, compounds of SBR,

polyurethane, silicone, polyacrylate, and Viton were tested. These data are shown in Table XV. When the report was issued (1962) the Viton samples had only been aged one year; consequently, no conclusions can be made. The others were stored 6 years and showed very good retention of properties. All would be considered serviceable after 6 years storage.

#### F. ROCK ISLAND ARSENAL

Rock Island Arsenal conducted a limited 3-year program to determine the effect of shelf storage on the properties of silicone, fluorosilicone, and fluorocarbon vulcanizates (10). The data showed that tensile strength, modulus, elongation, hardness, and resistance to volume change did not change significantly over the 3-year storage period (Table XVI). However, the report pointed out that small changes in properties due to mild aging may not be detectable from the above tests. Changes in strain (elongation measured under constant load) and compression set were considered to be more sensitive measures. The silicone and high strength silicone compounds showed a significant decrease in set after 3 years of storage; this was attributed to increased crosslinking with time. Further, the high strength silicone showed an appreciable decrease in strain which would be expected from additional crosslinking.

The fluorocarbon compound showed very little change in compression set from the original 38%. Maximum set of 50% was reached at 2 years of storage; however, specimens aged 3 years decreased to a set of 41%.

#### G. OKLAHOMA CITY AIR MATERIAL AREA (OCAMA)

Oklahoma City Air Material Area, Tinker Air Force Base, evaluated O-rings conforming to MIL-P-5516 and MIL-P-5315 that had been stored for periods as long as 13 years (11). Representative test results are shown in Tables XVII - XX. The data shown in these tables are not from the same batch of O-rings carried throughout the yearly periods of test. They represent individual values and are to be compared with original specification values since all batches tested were of specification quality. Contributory to variation in the values obtained are variation in aging conditions, variation between batches, and normal variation in test operation.

As expected, 100% modulus values of 5516 O-rings showed the greatest change, increasing as much as 61% after 10 years in one case. However, very little change in tensile strength was noted,

and elongation change averaged approximately -30% after up to 10 years. The OCAMA conclusion was that packaged O-rings conforming to MIL-P-5516 have a shelf life of at least 10 years under normal Air Force storage conditions.

Tables XXI and XXII show typical changes in physical properties of 5315 O-rings for two manufacturers after storage periods. In general, little change was noted, which again would indicate that under normal storage conditions the O-rings still would be usable after at least 10 years of storage.

#### H. MOBILE AIR MATERIAL AREA

Mobile Air Material Area, Brookley Air Force Base (12) tested materials conforming to MIL-P-5516 that had been stored for 7 years; these elastomers showed good retention of physical properties.

Typical data are in Tables XXIII and XXIV. This data coincides with that generated by OCAMA. Contributing to apparent variation in values obtained is the fact that differing batches of O-rings were involved, and the values cited do not follow a natural sequence from start to finish. Instead, since all the batches initially passed specification requirements, the comparison is made with these initial values, the changes over the storage periods then indicating trends and long term compliance with specification requirements. Specification materials covered by AMS-7270 (Table XXV), -7271 (Table XXVI), -7274 (Table XXVII), and MIL-P-5315 (Table XXVIII) were evaluated after 6 to 7 years storage. All were considered satisfactory as evidenced by the representative data shown in the tables. A recommendation was made that the shelf life of these specification materials be extended to 8 years.

As part of the same test program, 38 tests were run on overage material covered under MIL-R-7362, and only 7 passed. It was found that in most cases, the material met the original requirement but could not stand up under the 275°F test requirement. As a follow-up to this phase of the test program, Monsanto Research Corporation tested 3 sets of stored O-rings after 275°F aging. One set was 3 years old, another 7 years old, and the last 11 years old. The test data are shown in Table XXIX. The only O-rings to pass the heat aging requirement was the 3-year-old set; the others showed excessive decrease in elongation and were considered to have failed. These results are still not conclusive since the O-rings that failed were all from the same manufacturer. This is an area that should be further investigated.

#### I. COMPRESSION SET AGING STUDY - OCAMA

A long term compression set study of MIL-P-5516 O-rings is currently in progress at OCAMA. The program was started July 1964.

The O-rings, supplied by three different companies, were put under 30 percent compression and immersed in MIL-H-6083 hydraulic oil at 75°F. Periodically the O-rings are removed, measured, then put back under compression and reimmersed. The compression set data, expressed as a percentage of the original deflection, are shown in Table XXX.

The data show that an increase in compression set occurs with time, as would be expected. Further, there appears to be little difference in set resistance with supplier.

#### J. SOCIETY OF AUTOMOTIVE ENGINEERS (SAE)

Currently in progress is a fluorocarbon elastomeric O-ring aging study conducted by SAE. Four laboratories are participating in this study. The O-rings are evaluated after aging in the unconfined state and under 25 percent compression. Data through three years are shown in Table XXXI.

The data show that a wide divergence of values for the physical properties exist between the laboratories. The only trend noted in the data was the increase in compression set with aging and that the increase in set appears greater with the compressed O-rings. All other properties tested seem to have undergone minimum change through the three-year period.



A P P E N D I X

Figures 1 - 5

Tables I - XXVIII

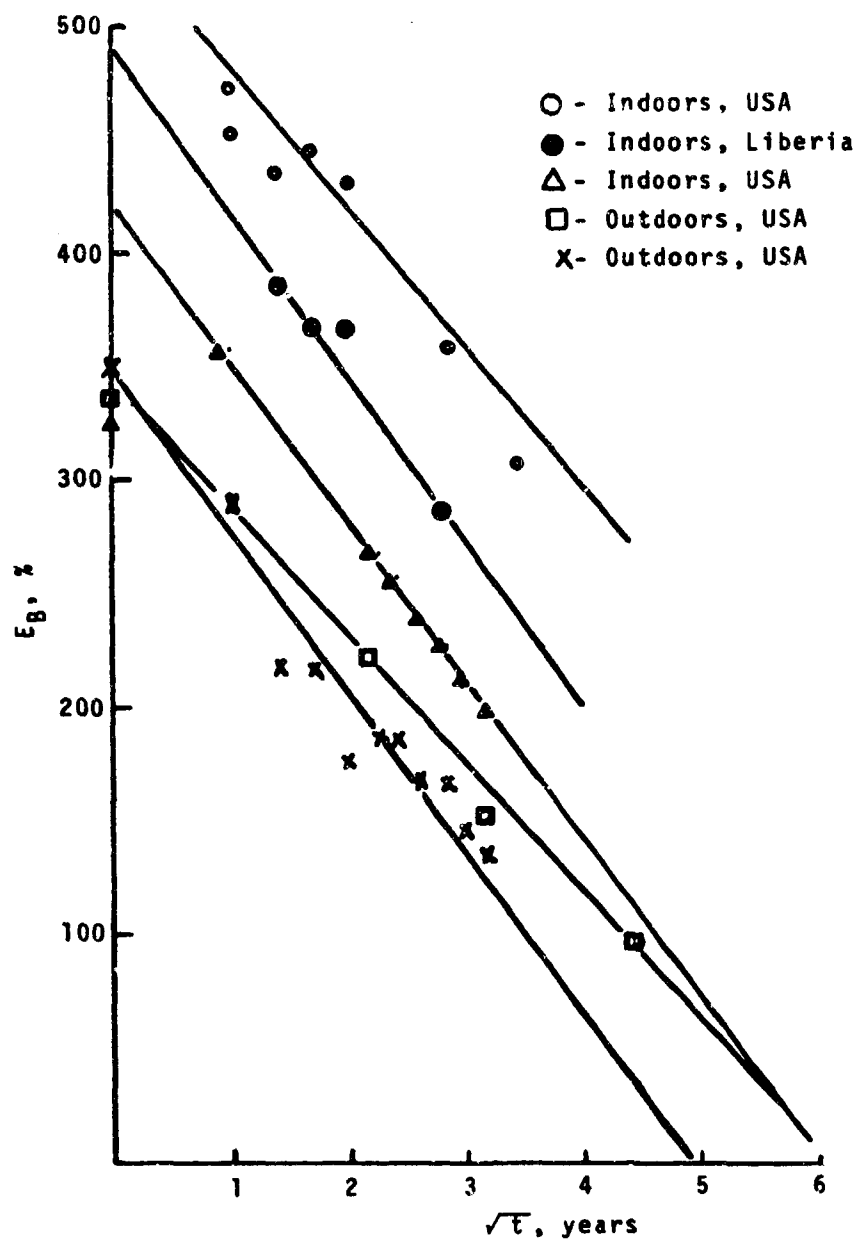


Figure 1. Neoprene: Effect of Aging on Elongation at Break ( $E_B$ ).

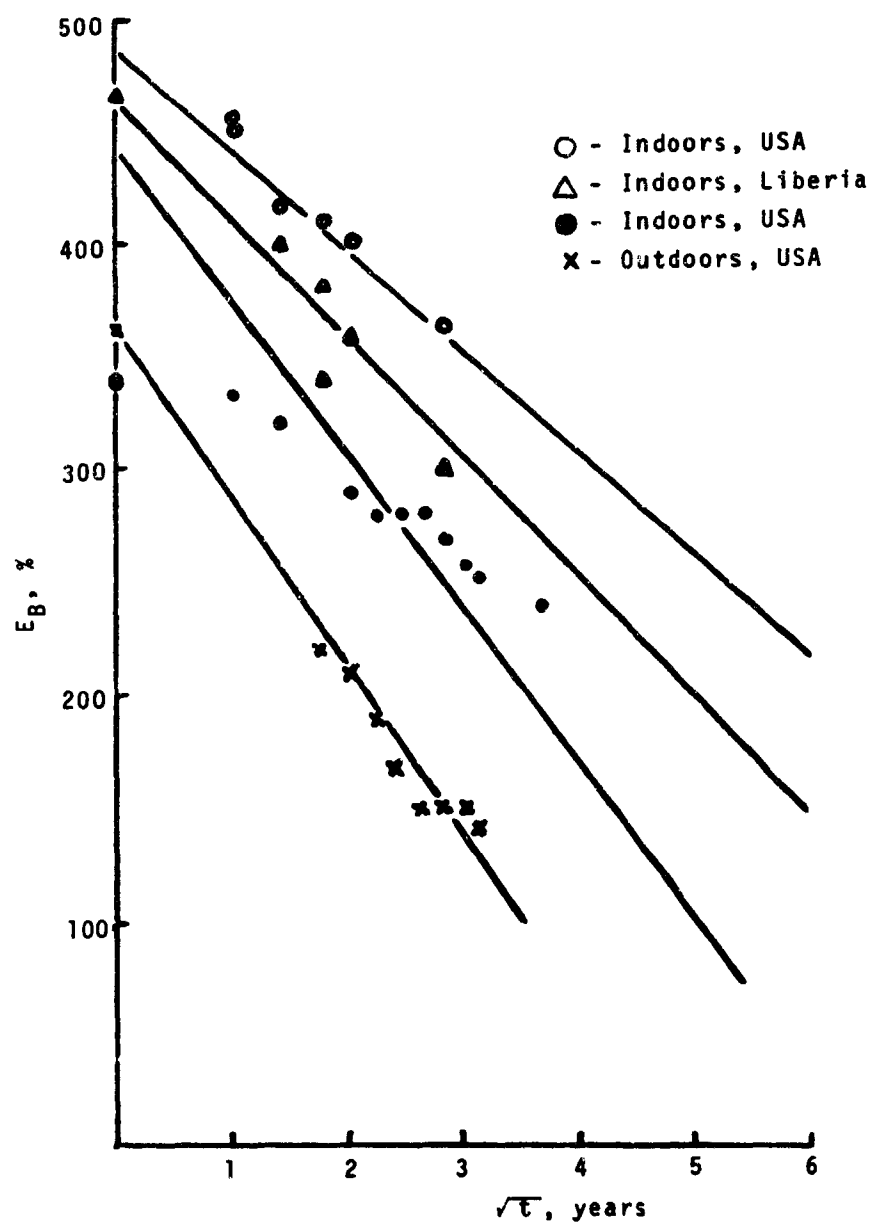


Figure 2. Nitrile: Effect of Aging on Elongation at Break ( $E_B$ ).

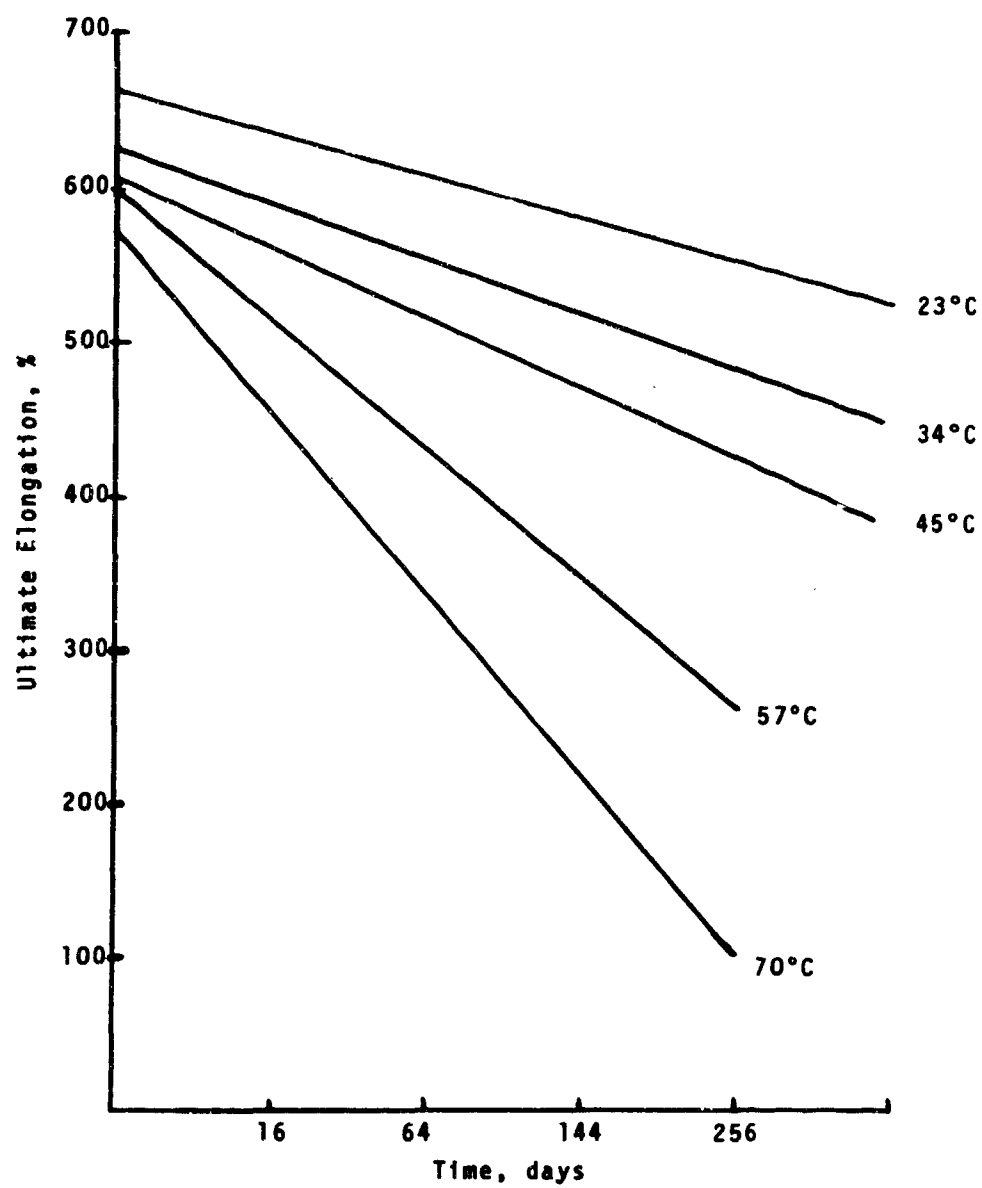


Figure 3. Effect of Aging at Various Temperatures on Ultimate Elongation.

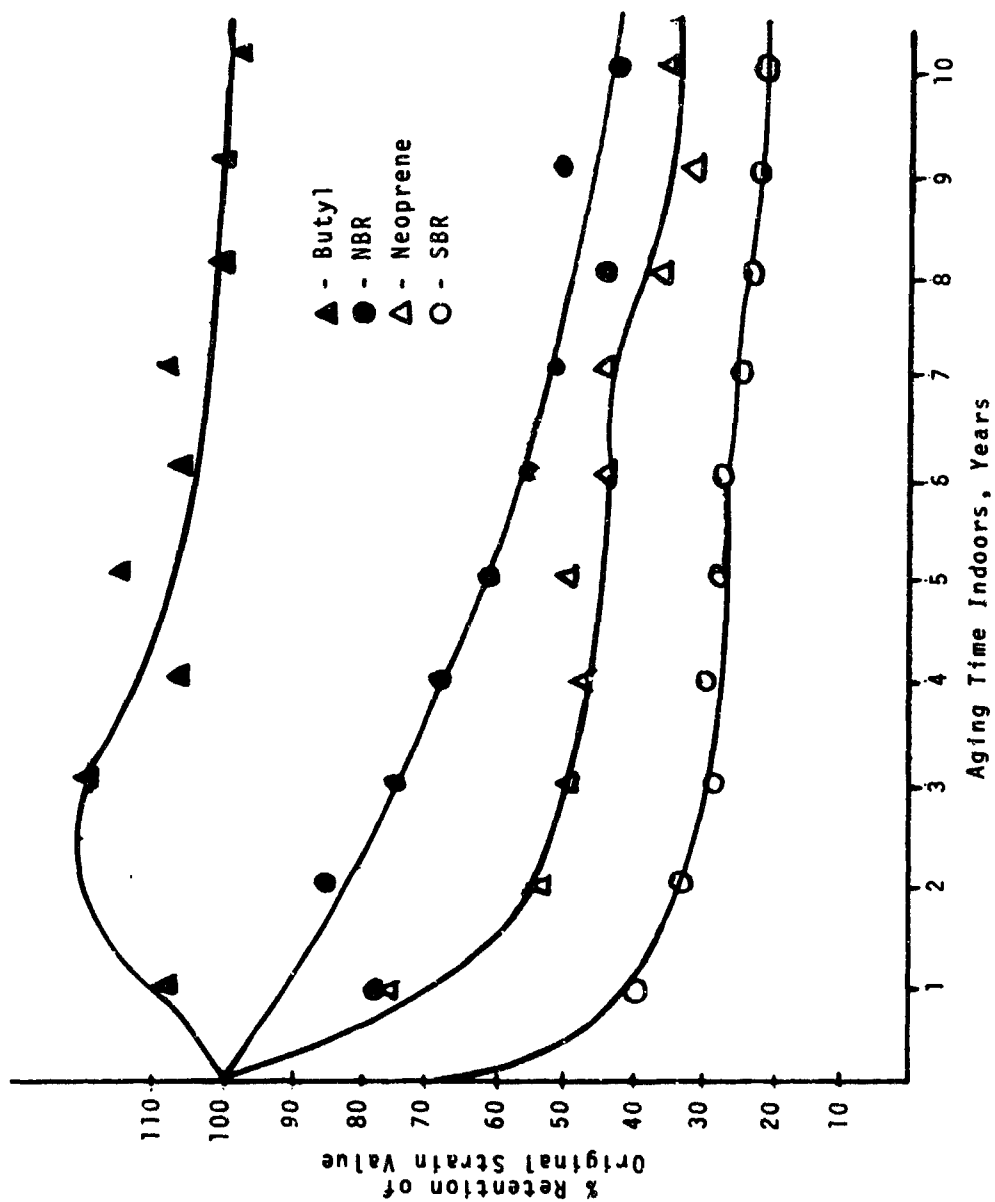


Figure 4. Percent Change in Strain With Time After Aging Indoors.

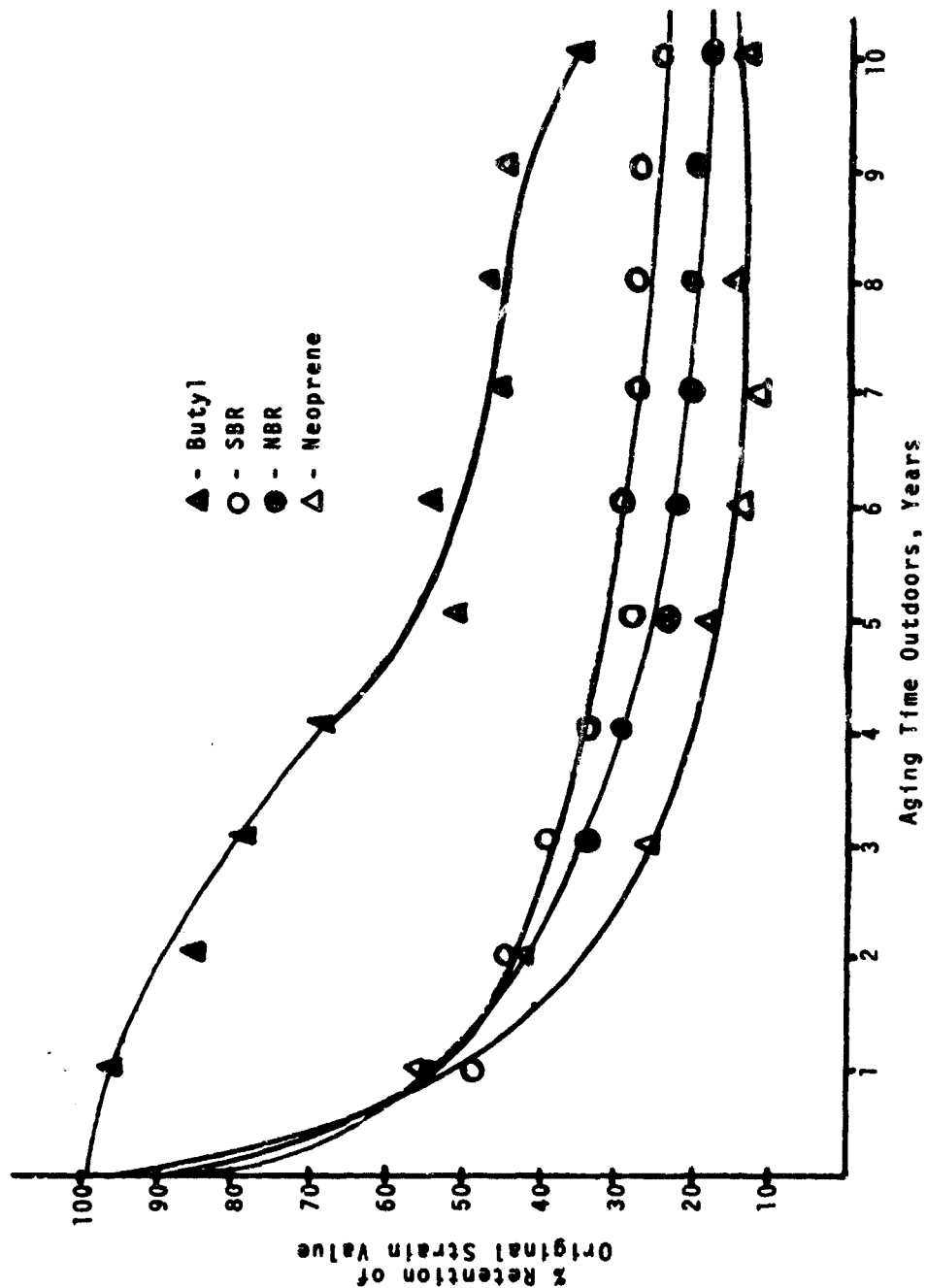


Figure 5. Percent Change in Strain With Time After Aging Outdoors.

TABLE I. PHYSICAL PROPERTIES OF VULCANIZATES AGED INDOORS  
TEN YEARS (PERCENT CHANGE FROM ORIGINAL VALUES)

Aging Time Periods	SBR			Neoprene			NBR			Butyl					
	T	E	H	T	E	H	T	E	H	T	E	H	S		
Original	1930	420	56	149	330	53	68	1370	340	64	74	1910	720	45	199
1 year	+24	-7	+16	-60	+6	+28	-25	+3	-2	+9	-22	+9	+15	+2	+9
2 years	+29	-12	+27	-66	-6	+42	-47	+12	-6	+16	-17	+7	+18	+11	+24
3 years	+12	-21	+11	-71	-3	+25	-50	+7	0	+8	-26	-8	+13	-1	+21
4 years	+21	-24	+18	-70	-21	+38	-52	+27	-15	+9	-31	+10	+18	+2	+5
5 years	+17	-26	+18	-71	-18	+36	-50	+32	-18	+11	-39	+11	+8	0	+16
6 years	+4	-36	+18	-71	-21	+36	-54	+28	-18	+11	-43	+10	+14	-4	+5
7 years	+16	-29	+23	-73	-30	+36	-54	+35	-18	+13	-49	+7	+10	0	+7
8 years	-1	-38	+21	-75	-21	+36	-62	+32	-21	+13	-53	+4	+11	+7	+1
9 years	+15	-38	+23	-75	-36	+42	-66	+16	-24	+14	-49	+1	+7	+7	+1
10 years	+15	-41	+21	-75	-39	+42	-63	+45	-26	+16	-54	+10	+7	+7	-3

NOTE: T = Tensile, psi  
E = Ultimate Elongation, %  
H = Hardness, Shore A  
S = Strain, % Elongation @ 200 psi Load

TABLE II. PHYSICAL PROPERTIES OF VULCANIZATES AGED OUTDOORS  
TEN YEARS (PERCENT CHANGE FROM ORIGINAL VALUES)

Aging Time Periods	SBR			Neoprene			NBR			Butyl					
	T	E	H	T	E	H	T	E	H	T	E	H	S*		
Original	2040	480	57	105	350	59	70	1520	360	63	83	2420	870	44	101
1 year	+19	-23	+14	-51	-17	+15	-43	+2	-17	+16	-45	-11	-3	+7	-4
2 years	+6	-29	+26	-55	-37	+34	-57	+1	-22	+30	-55	-15	-8	+20	-10
3 years	-11	-40	+14	-60	-37	+27	-73	-18	-39	+25	-65	-19	-11	+18	-21
4 years	+1	-46	+26	-67	-40	+41	-71	+8	-42	+32	-70	-11	-8	+30	-31
5 years	+5	-50	+25	-71	-32	+39	-81	-8	-47	+33	-74	-15	-14	+25	-48
6 years	+9	-48	+16	-69	-37	+32	-86	-5	-53	+27	-76	-8	-12	+16	-43
7 years	+18	-50	+28	-71	-30	+41	-87	-9	-58	+33	-78	-8	-17	+34	-52
8 years	+5	-50	+30	-71	-34	+41	-83	-12	-58	+35	-77	-11	-17	+32	-51
9 years	+12	-54	+30	-71	-31	+42	-77	+5	-58	+33	-77	-10	-21	+39	-52
10 years	+7	-56	+33	-73	-37	+49	-84	-3	-61	+38	-80	-7	-23	+41	-55

NOTE: T = Tensile, psi  
E = Ultimate Elongation, %  
H = Hardness, Shore A  
S = Strain, % Elongation @ 200 psi Load  
\*S = Strain, % Elongation @ 100 psi Load



TABLE III. STRAIN DATA FOR HEAT AGED VULCANIZATES

(Vulcanizates Aged in an Air Oven @ 158°F) (4)

Aging Time Period (Days)	% Retention of Original (Unaged) Value			
	<u>SBR</u>	<u>Neoprene</u>	<u>NBR</u>	<u>Butyl</u>
1	87	99	99	107
3	74	96	93	100
5	69	94	87	85
7	64	91	82	80
10	59	88	76	72
20	50	81	58	62
28	50	75	52	56
38	44	74	41	53
50	36	63	31	
127	27	41	19	
160	30	34	21	
223	24	29	12	
338	19	21	16	
419	16	20		

TABLE IV. STRAIN DATA FOR INDOOR AGED VULCANIZATES (4)

Aging Time Period (Years)	% Retention of Original (Unaged) Value			
	<u>SBR</u>	<u>Neoprene</u>	<u>NBR</u>	<u>Butyl</u>
1	40	75	78	109
2	34	53	83	124
3	29	50	74	121
4	30	48	69	105
5	29	50	61	116
6	29	46	57	105
7	27	46	53	107
8	25	38	47	100
9	25	34	51	100
10	25	37	46	97

TABLE V. STRAIN DATA FOR OUTDOOR AGED VULCANIZATES (4)

Aging Time Period (Years)	% Retention of Original (Unaged) Value			
	<u>SBR</u>	<u>Neoprene</u>	<u>NBR</u>	<u>Butyl</u>
1	49	57	55	96
2	45	43	45	85
3	40	27	35	79
4	34	29	30	69
5	29	19	26	52
6	31	15	24	57
7	29	13	22	48
8	29	17	23	49
9	29	23	23	48
10	27	16	20	35

TABLE VI. PHYSICAL PROPERTY CHANGE OF COMMERCIAL  
NITRILE COMPOUNDS - RMA

Storage Age (Years)	Tensile Change (%)	Elongation Change (%)	100% Modulus Change (%)	Hardness Change (points)
2	+0.5	-7.4	0	+3
	+0.1	-6.3	+5.7	+2
	-2.6	-5.4	+53.0	+2
4.75	+0.4	-12.4	+17.5	+3
	+6.8	-7.7	-	+5
	+3.6	-8.5	+26.4	+5
7	+1.0	-16.1	+23.6	+7
	+7.7	-13.0	-	+4
	+3.6	-8.5	+23.4	+3

TABLE VII. PHYSICAL PROPERTY CHANGE OF COMMERCIAL  
NEOPRENE COMPOUNDS - RMA

Storage Age (Years)	Tensile Change (%)	Elongation Change (%)	100% Modulus Change (%)	Hardness Change (points)
1.25	-0.8	-20.6	+56.2	+4
	-0.8	-11.0	+43.1	+9
	-1.3	-14.9	+24.3	+6
2.75	-11.4	-25.5	+62.5	+5
	+11.3	-8.7	+15.1	+7
	+0.3	-17.2	+76.4	+9
	0	-19.1	+52.0	+7
7	-8.9	-19.7	+33.2	+10
	-0.1	-22.8	+51.4	+8
7.75	-22.7	-41.0	+125	+10

TABLE VIII. PHYSICAL PROPERTY CHANGE OF BUTYL RUBBER COMPOUNDS - RMA

<u>Storage Age (Years)</u>	<u>Tensile Change (%)</u>	<u>Elongation Change (%)</u>	<u>100% Modulus Change (%)</u>	<u>Hardness Change (points)</u>
1.75	+0.9 +3.1 -11.5	-25.9 -4.7 -20.1	-28.1 +6.3 +12.0	+5 0 +1
2.75	-4.3 +4.7 -4.5	-24.5 -8.5 -10.2	+34.4 +5.7 +17.8	+5 0 0
4	+10.4 -6.5	-24.8 -10.3	+62.5 -11.8	+10 -1
5.75	+12.2	-28.0	+87.5	+10
7.75	+13.0	-24.2	+62.5	+10

TABLE IX. PHYSICAL PROPERTY CHANGE - MIL-P-5516, CLASS B - RMA

<u>Storage Age (Years)</u>	<u>Tensile Change (%)</u>	<u>Elongation Change (%)</u>	<u>100% Modulus Change (%)</u>	<u>Hardness Change (points)</u>
1	+0.7 +10.0	+4.7 -6.7	+8.0	+1 +5
2.25	+4.3 +0.9	-4.2 -10.2	+20.7 +34.6	+2 +5
4	-0.3 +6.4	-2.3 -8.4	+18.6 +38.1	+2 +10
5.75	-5.0 +6.5	-23.7 -18.1	+64.4 +73.8	+13 +10
7.5	+17.0	-20.0	+41.0	+10
7.75	+15.3	-18.6	+78.5	+10

TABLE X. PHYSICAL PROPERTY CHANGE - MIL-G-5510A  
AND MIL-P-5315A COMPOUNDS - RMA

Storage Age (Years)		Tensile Change (%)	Elongation Change (%)	100% Modulus Change (%)	Hardness Change (points)
1	(1)*	+9.0	-33.0	-	0
	(2)	+23.0	+6.0	-	+6
2	(1)	+11.0	-26.0	-	-1
	(2)	+23.0	+12.0	+4.0	+4
3.5	(1)	+14.0	-20.0	-	-1
	(2)	+21.0	-4.0	+29.0	+1
4.5	(1)	+17.5	-37.0	-	0
	(2)	+18.0	-12.0	+44.0	+2
7.5	(1)	+17.0	-41.0	-	+2
	(2)	+16.0	-11.0	+34.0	+9

\*(1) MIL-G-5510A  
(2) MIL-P-5315A

TABLE XI. PHYSICAL PROPERTY CHANGE - MIL-P-25732  
AND MIL-P-18017 COMPOUNDS - RMA

Storage Age (Years)		Tensile Change (%)	Elongation Change (%)	100% Modulus Change (%)	Hardness Change (points)
1	(1)*	-5.1, +1.1	+3.6, -10.0	-4.0	+4, +7
	(2)	+11.0	-10.0	-	+8
3	(1)	-2.2	-7.5	+14.9	+7
4.5	(2)	+17.0	-13.0	+54.0	+14
5	(1)	+0.2	-12.1	+33.8	+8
5.5	(2)	+17.0	-13.0	+64.0	+11
7.5	(2)	+19.0	-23.0	+72.0	+15

\*(1) MIL-P-25732  
(2) MIL-P-18017

TABLE XII. PHYSICAL PROPERTY CHANGE OF OVERAGE O-RINGS  
MANUFACTURER'S DATA

Manufacturer	Age	Spec.No.	Tensile (psi)	Elongation (%)	Modulus 100%	Hardness
1	New	MIL-P-5516	1345	203	534	70
	5 Years	"	1430	171	693	73
	% Change		+6	-15.6	+30	+3
2	New	MIL-P-5516	1485	195	693	70
	5.5 Years	"	1520	195	825	72
	% Change		+2.3	0	+19	+3
3	New	MIL-P-5516	1485	222	462	68
	5.25 Years	"	1550	168	775	70
	% Change		+4.5	-24	+68	+5
4	New	MIL-P-5516	1500	225	675	69
	7.5 Years	"	1840	185	1025	80
	% Change		+23	-18	+52	+16
5	New	MIL-P-5315	1500	282	375	61
	5.5 Years	"	1560	250	430	61
	% Change		+4	-11	+23	0
6	New	MIL-P-5315	1515	260	345	60
	5 Years	"	1715	244	462	60
	% Change		+11.6	-6.2	+25	0
7	New	MIL-P-5315	1465	260	410	61
	7.5 Years	"	1800	230	600	71
	% Change		+23	-11	+46	+16

TABLE XIII. PHYSICAL PROPERTY CHANGE OF OVERAGE O-RINGS  
MANUFACTURER'S DATA

Age	Spec. No.	Hardness	Tensile (psi)	Elongation (%)	Volume	Volume Change Type I Fuel MIL-S-3136A	Specific Gravity	Exposure Conditions
New	AMS7274	75	1558	288				None
5-3/4 Years	"	79	1320	208				
% Change	"	5	-15	-28				
New	"	2	6.3	-20.1	3.2			90 hr 300°F*
5-3/4 Years	"	1	-5	-23.1	1			ASTM 1 Oil
								% Change
New	"	-11			32.4			70 hr 300°F*
5-3/4 Years	"	-12			29.8			ASTM 3 Oil
								% Change
New	"	8	-14.1					70 hr 212°F*
5-3/4 Years	"	5	13.8					Air
								% Change
New	AMS7274	75	1558	288				None
7-1/4 Years	"	80	1594	168				
% Change	"	7	2	-42				
New	"	2	6.3	-20.2	3.2			90 hr 300°F*
7-1/4 Years	"	1	-21.4	-25.6	1.3			ASTM 1 Oil
								% Change
New	"	-11			32.4			70 hr 300°F*
7-1/4 Years	"	-12			28.2			ASTM 3 Oil
								% Change
New	"	8	-14.1					70 hr 212°F*
7-1/4 Years	"	5	-11.6					Air
								% Change
New	MIL-P-5315 <sup>a</sup>		1227	389		6.3	1.116	None
5-1/4 Years	"		1293	283		5.7	1.139	
% Change	"		5	-27		-10	2	
New	MIL-P-5315 <sup>b</sup>		1149	330		5.5	1.121	None
5-1/4 Years	"		1241	246		5.5	1.139	
% Change	"		8	-25		0	1.6	

\*In addition to normal aging

<sup>a</sup>Manufacturer A

<sup>b</sup>Manufacturer B

TABLE XIV. EFFECT OF SHELF AGING ON MIL-P-5516 O-RINGS -  
MARE ISLAND NAVAL SHIPYARD

Storage Age (Years)	Ultimate Tensile (psi)			Ultimate Elongation (%)			100% Modulus (psi)		
	A	B	C	A	B	C	A	B	C
<u>First Manufacturer</u>									
4	1600			140			1090		
5	1590	1570	1560	150	150	140	1020	1010	1050
6	1630	1570	1610	140	140	140	1140	1090	1080
7	1550	1550	1580	130	130	140	1130	1150	1130
8	1560	1590	1560	140	130	140	1110	1180	1080
<u>Second Manufacturer</u>									
4	1730			150			980		
5	1630	1770	1770	150	160	150	960	1000	980
6	1760	1750	1740	150	150	150	1010	1050	980
7	1750	1760	1760	150	140	150	1110	1120	1090
8	1750	1770	1640	150	160	160	1050	1080	850

A - O-Rings stored in sealed envelopes.

B - O-Rings exposed to air and artificial light.

C - O-Rings exposed to air but light excluded.



TABLE XV. PHYSICAL PROPERTIES OF AGED VULCANIZATES - PRECISION RUBBER

Aging Time (years)	SBR			Polyurethane			Silicone			Polyacrylate			Viton							
	T	E	H	T	E	H	T	E	H	T	E	H	T	E	H	C				
Original	1500	200	68	41	3200	475	71	92	800	80	70	10	1300	205	70	35	2000	320	75	3
1	1500	200	69	42	3000	360	78	97	850	85	77	10	1350	255	64	28	2100	315	77	4
2	1450	180	70	45	3100	310	77	97	900	80	76	14	1400	345	64	24				
3	1375	170	71	44	3400	340	77	80	860	70	78	12	1475	325	72	24				
4	1425	170	72	38	3450	350	78	85	850	75	78	8	1450	345	72	26				
5	1400	170	72	36	3475	360	78	82	920	70	78	8	1500	305	68	30				
6	1450	160	72	36	-	-	-	-	1000	80	78	8	1500	280	68	30				

NOTE: T = Tensile, psi

E = Ultimate Elongation, %

H = Hardness, Shore A

C = Compression Set, % - Test conditions not specified

TABLE XVI. THE EFFECT OF SHELF STORAGE LIFE ON THE PHYSICAL PROPERTIES OF SILICONE, FLUOROSILICONE, AND FLUOROCARBON VULCANIZATES - ROCK ISLAND ARSENAL

Shelf Storage Time (Years)	Tensile Strength (psi) ASTM D 412 (avg of 3)	Modulus at 300% E (psi) ASTM D 412 (avg of 3)	Elongation (%) ASTM D 412 (avg of 3)	Hardness (Shore A) ASTM D 676 (avg of 5)	Strain, NBS, 400 psi (%) ASTM D 1456 (avg of 2)	Compression Set 22 hr/347°F (%) ASTM D 395 (avg of 2)	Volume Change 70 hr/302°F ASTM #3 Oil (%) ASTM D 471 (avg of 2)
<b>Fluorocarbon</b>							
Original	2280	1810	380	69	127	38	7
0.5	2330 (+2)	1660 (-8)	410 (+8)	70	127 (0)	44	6
1.0	2650 (+16)	1730 (-4)	470 (+24)	72	129 (+2)	48	5
1.5	2460 (+8)	1680 (-7)	460 (+21)	71	121 (-5)	48	7
2.0	2610 (+14)	1730 (-4)	450 (+18)	70	130 (+2)	50	6
3.0	2520 (+11)	1720 (-5)	460 (+21)	70	115 (-9)	41	3
<b>Silicone</b>							
Original	840	720	400	54	106	49	41
0.5	910 (+8)	890 (+24)	370 (-8)	53	103 (-3)	50	43
1.0	1010 (+20)	870 (+21)	380 (-5)	57	101 (-5)	42	42
1.5	970 (+15)	850 (+18)	370 (-8)	54	98 (-8)	43	44
2.0	1030 (+23)	930 (+29)	350 (-13)	54	100 (-6)	38	45
3.0	940 (+12)	870 (+21)	350 (-13)	54	99	21	43
<b>High Strength Silicone</b>							
Original	1610	310	740	50	218	62	109
0.5	1650 (+2)	390 (+26)	670 (-9)	50	203 (-7)	61	114
1.0	1680 (+4)	420 (+35)	700 (-5)	51	194 (-11)	61	104
1.5	1610 (0)	470 (+52)	630 (-15)	52	186 (-15)	58	107
2.0	1650 (+2)	430 (+39)	660 (-11)	50	197 (-10)	55	103
3.0	1560 (-3)	410 (+32)	650 (-12)	51	181 (-17)	30	103
<b>Fluorosilicone</b>							
Original	1100	910	360	58	98	16	7
0.5	1130 (+3)	940 (+3)	370 (+3)	57	95 (-3)	14	5
1.0	1170 (+6)	870 (-4)	400 (+11)	59	98 (0)	12	7
1.5	1180 (+7)	940 (+3)	400 (+11)	55	101 (+3)	11	7
2.0	1220 (+11)	1000 (+10)	370 (+3)	58	94 (-1)	11	6
3.0	1180 (+7)	940 (+3)	390 (+8)	60	91 (-7)	5	5

(Parenthetical values are percent change from original.)

TABLE XVII. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
OCAMA - MIL-P-5516 - MANUFACTURER A

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>100% Modulus</u>	<u>Volume Swell (%)</u>
2	764	176	600	6.0
	1123	201	644	
	1279	152	612	
	1107	177	753	
7	1281	82	1053	5.5
	1432	153	1071	11.3
	1233	153	995	9.2
	1445	109	1059	5.9
	1411	134	1042	7.9
8	1356	135	1040	-
	1404	141	1061	
	1407	143	1037	
	1414	147	1018	
	1404	146	1057	
9	1033	119	792	11.0
	1347	164	815	
	1505	181	839	

TABLE XVIII. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
OCAMA - MIL-P-5516 - MANUFACTURER B

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>100% Modulus</u>	<u>Volume Swell (%)</u>
3	1480	202	599	3.1
	1642	216	636	3.6
	1581	223	589	6.3
	1642	228	608	
5	1607	168		8.2
	1572	168		5.4
	1519	166		6.8
	1589	176		6.9
	1554	170		6.1
	1446	209	570	6.8
	1453	187	660	7.1
7	1672	146	1039	
	1191	123	983	
	1463	140	942	
	1403	135	972	
	1411	138	962	
	1637	156	977	
	1454	143	910	
	1005	97	-	
	1582	137	1062	
	1615	160	930	
10	1061	107	964	15.9
	1574	166	950	7.3
	1120	135	815	9.1
	1147	120	950	16.9
	1243	134	849	5.8
	1366	151	881	5.6
	1167	142	772	4.1
	1275	149	810	
	1467	151	978	
	1329	152	819	
13	1438	134	957	12.3

TABLE XIX. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
OCAMA - MIL-P-5516 - MANUFACTURER C

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>100% Modulus</u>	<u>Volume Swell (%)</u>
2	1748	209	617	3.2
	1691	197	625	
	1694	217	559	
	1628	200	609	
	1697	202	587	
3	1749	190	737	4.4
	1535	190	654	
	1601	181	631	
	1611	197	675	
		184	649	
5	1791	179	827	9.4
	1709	156	890	
6	1627	171	761	7.5
	1398	151	752	7.8
	1341	144	770	9.1
	1684	183	776	6.2
		197		7.6
7	1447	130	1026	9.4
	1558	133	1016	
	1551	144	960	
	1737	145	1041	
	1684	143	1024	

TABLE XX. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
OCAMA - MIL-P-5516 - MANUFACTURER D

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>100% Modulus</u>	<u>Volume Swell (%)</u>
5	1826	216	635	7.1
	1970	236	602	
	1974	228	651	
	1932	228	640	7.2
	1952	232	618	7.2
	1222	151	671	6.9
	1761	214	645	7.0
	1767	216	608	6.9
7.5	1707	222	640	8.6
	1698	222	645	8.8
	1629	218	617	8.8
	1682	218	639	8.6
	1769	246	590	8.6
	2059	229	675	9.1
	1418	166	733	
	1636	196	686	
	1753	210	685	
	1515	180	707	
	1782	218	710	
9	1790	187	820	
	1630	172	822	
	1688	180	776	
	1212	134	812	7.3
	1317	142	852	
	1732	178	824	
	1789	191	801	
10	1879	202	765	8.3
	1818	195	762	
	1976	193	830	
	1717	176	778	
	1970	196	796	

TABLE XXI. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
OCAMA - MIL-P-5315 - MANUFACTURER A

Storage Age (years)	Ultimate Tensile (psi)	Ultimate Elongation (%)	100% Modulus	Volume Swell (%)	
				High	Low
5	1783	258	519	-	3.9
	1822	254	525	33.2	-
	1966	282	534	-	3.7
6	1744	203	505	-	7.4
	1810	277	512	39.1	-
	1804	274	535	-	-
7	1489	273	429	37.8	5.6
	1210	186	500	37.5	5.8
	1443	205	531	-	-
	1460	238	510	-	-
10	1672	262	519	37.4	6.9
	1682	262	529	-	-
	1721	285	506	-	-
	1319	200	524	-	-
	1713	245	577	-	-
11	1646	250	504	-	6.5
	1704	252	526	40.6	-

TABLE XXII. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
OCAMA - MIL-P-5315 - MANUFACTURER B

Storage Age (years)	Ultimate Tensile (psi)	Ultimate Elongation (%)	100% Modulus	Volume Swell (%)	
				High	Low
5	1501	259	434	-	5.9
	1531	259	449	38.0	-
	1651	286	437	-	-
	1508	265	405	-	6.0
	1532	257	456	37.9	-
6.5	1289	189	543	-	-
	950	139	585	41.2	6.6
	1073	166	576	-	-
7	1653	273	417	-	3.9
	1643	206	612	37.9	-
	1533	233	471	-	3.1
	1564	195	618	34.3	-
10	1687	264	492	-	5.7
	1640	236	542	36.8	-



TABLE XXIII. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
MOBILE - MIL-P-5516 - MANUFACTURER A

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>100% Modulus</u>	<u>Volume Change (%)</u>
5	1286	130	-	1.4
	1333	175	766	6.9
	1263	120	982	6.8
6	1233	130	985	6.3
	1200	150	800	9.7
	1286	130	1160	3.5
	1344	160	880	5.8

TABLE XXIV. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
MOBILE - MIL-P-5516 - MANUFACTURER B

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>100% Modulus</u>	<u>Volume Change (%)</u>
5	1493	180	716	4.9
	1132	130	712	7.1
	1433	130	980	8.8
	1667	120	1502	4.9
6	1655	130	1288	5.9
	1773	130	1288	7.1
	1325	150	735	6.6
	1382	140	882	7.7
	1647	180	747	7.1
	1850	125	-	5.9
	1018	100	1018	9.1
7	1533	180	867	5.2
	1310	125	1120	7.3

TABLE XXV. O-RING PHYSICAL PROPERTIES AFTER STORAGE - MOBILE - AMS-7270

	Required	Manufacturers										
		E	C			B						
Hardness	70 ± 5	72	69	73	71	70	71	75	70	74	75	
Tension (Min.)	1500	2200	1933	1410	1771	1500	1666	1833	1600	1533	1733	
Elongation, % (Min.)	150	170	270	230	270	160	220	300	240	225	225	
Fuel B (168 hr @ RT)												
Hardness Change	-25	-7	-4	-5	-8	-10	-4	-10	-4	-5	-7	
Tensile Change (%)	-65	-49	-39	-38	-21	-56	-52	-51	-65	-10	-38	
Elongation Change (%)	-55	-48	-33	-41	-32	-43	-48	-43	-55	-22	-55	
Volume Change	+40	+38	+3	+36	+35	+9	+21.2	+10	+27	+23	+28	
Fuel A & B Volume	-8	-1	-5	-6	-3	-5	+1	-5	-2	0	-6	
ASTM #3 Oil (70 hr @ 300°F)												
Hardness	-25	-16	-7	-11	-13	-13	-8	-12	-10	-8	-7	
Volume Change	+35	+28.4	+19.5	+25	+27	+16	+18	+16	+15	+32	+22	
Air Oven (70 hr @ 212°F)												
Hardness	+10	+9	+3	+5	+1	0	+3	0	+6	+4	+2	
Tensile (%)	-25	-25	+26	+16	+6	-8	+6	0	+8	+8	+6	
Elongation (%)	-40	-40	0	-4	0	-22	0	-25	-19	-12	-6	
Low Temperature -	No Crack	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	
Storage Age, Years		6	6	5	6	5	6	6	6	5	4	

TABLE XXVI. O-RING PHYSICAL PROPERTIES AFTER STORAGE - MOBILE - AMS-7271

Original	Required	Manufacturers		
		B	F	G
Hardness	65 ± 5	70	63	66
Tensile, psi	1200	1260	1600	1588
Elongation, %	200	275	210	210
Fuel B				300
Volume Change, %	+40 +70	+50	+47	+41
Fuel A				+46
Volume Change, %	>0	OK	OK	OK
Low Temperature Flex		OK	OK	OK
Air Oven Resistance				
Hardness Change	+15	+2	+3	+2
Tensile Change (%)	-25	+10	-11	-4
Elongation Change (%)	-50	-8	-24	-20
Bend 180°	No crack	OK	OK	OK
Storage Age, Years		6	4	6
				6

TABLE XXVII. O-RING PHYSICAL PROPERTIES AFTER STORAGE - MOBILE - AMS-7274

	Required	Manufacturers									
		B	D		A						F
Hardness	70 ± 5	73	74	72	73	70	71	69	69		
Tensile, psi	1500	1500	2000	2200	2030	1667	1815	1567	1533		
Elongation, %	150	210	325	300	290	200	215	210	240		
ASTM #1 Oil (96 hr @ 300°F)											
Hardness Change	-5 +10	+2	-4	-4	-1	-2	-2	-2	+6		
Tensile Change (%)	-60	-15	-13	-19	-12	0	0	0	+9		
Elongation Change (%)	-50	-18	-27	-31	-20	-4	-8	-4	+12		
Volume Change (%)	+10	+2.4	+2.7	+2.9	+3	-2.1	+1.8	+2	+4.5		
ASTM #3 Oil (70 hr @ 300°F)											
Hardness Change	-20 0	-6	-12	-13	-16	-10	-11	-10	-3		
Volume Change (%)	+25 +45	+32	+31	+33	+34.6	+41	+39.4	+40	+15		
Air Oven (70 hr @ 212°F)											
Hardness Change	+10	-12	+4	+1	+1	+2	+2	+2	+6		
Tensile Change (%)	-25	+17	+6	+16	+8	+4	+6	+5	+2		
Elongation Change (%)	-40	0	-30	0	0	-6	-3	-6	-		
Bend Flat	No Crack	OK	OK	OK	OK	OK	OK	OK	OK		
Storage Age, Years		6	5	6	6	7	7	7	7		

TABLE XXVIII. O-RING PHYSICAL PROPERTIES AFTER STORAGE -  
MOBILE - MIL-P-5315 - MANUFACTURER A

<u>Storage Age (years)</u>	<u>Ultimate Tensile (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>Hardness</u>	<u>Volume Change</u>	
				<u>High</u>	<u>Low</u>
1	1700	290	65	28.1	0.01
5	1600	230	62	29	0.8
	1600	275	66	30	0.06
	1460	225	70	30.6	0.10
	1533	225	66	30.5	1.2
6	1254	180	62	28.4	2.1
	1558	215	65	31.4	2.6
	1492	210	62	29.3	1.1
	1357	240	64	28.7	1.0
	1643	225	70	30.5	2.1
7	1412	200	73	25.3	0.8
	1665	275	66	30.5	4.5

TABLE XXIX. STORED O-RING PHYSICAL PROPERTY CHANGE AFTER  
OVEN AGING - MONSANTO - MIL-R-7362 O-RINGS

	<u>Required</u>	<u>Manufacturer D</u>		<u>Manufacturer A</u>
Tensile Change, % Maximum	-20	+31	-36	+31
Elongation Change, % Maximum	-70	-75	-87	-52
Hardness	-	+28	+26	+15
Volume Change, %	-20	-16	-14.5	-10
Storage Age, Years		7	11	3

TABLE XXX. LONG TERM COMPRESSION SET TEST

Manufacturer	1 Month	2 Months	3 Months	4 Months	6 Months	1 Year	2 Years
C	7.44	8.43	9.92	10.74	12.2	13.2	16.50
	7.56	8.40	10.08	11.09	12.8	13.6	15.97
	8.40	8.40	8.91	10.08	11.9	13.4	15.13
	6.84	8.21	9.40	9.40	11.5	13.0	15.38
	6.84	6.96	8.52	9.04	11.0	12.0	13.04
Median	7.44	8.40	9.40	10.08	11.9	13.2	15.38
D	4.76	5.87	7.14	8.73	10.6	12.5	14.29
	4.84	6.13	7.90	9.19	11.3	12.9	16.49
	5.47	6.41	7.19	8.90	10.9	13.3	14.84
	3.91	5.94	6.88	7.81	10.2	12.2	13.28
	3.98	6.87	7.63	8.54	11.0	12.8	13.74
Median	4.76	5.13	7.19	8.73	10.9	12.8	14.29
A	7.04	8.02	8.64	9.25	10.5	12.3	12.96
	6.17	7.16	8.40	9.25	10.5	12.2	12.96
	6.92	8.18	9.18	10.06	11.9	13.3	14.21
	6.14	7.36	7.98	9.20	11.0	11.8	15.50
	6.25	7.50	9.38	10.12	12.4	12.6	13.13
Median	6.25	7.50	8.64	9.25	11.0	12.3	13.13

NOTE: The compression set is expressed as the percentage of the original deflection.



NOTE: Compression fixture containing 2 O-Rings which had been stored at room temperature for three years was placed in an oven for 22 hrs at 392°F. Set was measured 30 mins and 3 days after O-Rings were removed from the fixture.

Comp. Set, %  
22 hrs at 392°F  
30 min. after release  
3 days after release

## REFERENCES

1. J. Mandel, et al., "Measurement of the Aging of Rubber Vulcanizates," Proceedings International Rubber Conference, Washington, D. C., November 1959.
2. A. L. Stokoe, "Estimation of Service Life of Neoprene and Nitrile Rubbers: A Review," Explosive Research and Development Establishment, Technical Memorandum No. 2/M/64 (AD No. 452124).
3. A. Cosgarea, et al., "Aging of Cure Dated Items and Various Elastomeric Compounds," University of Oklahoma Research Institute, Final Report, Contract AF 34(601)-14089, September 1963.
4. E. W. Bergstrom, "Indoor and Outdoor Aging of Elastomeric Vulcanizates Over a Ten Year Period," Rock Island Arsenal Laboratory, Report No. 61-3868, October 1961.
5. E. W. Bergstrom, "Six Year Indoor and Outdoor Aging of Elastomeric Vulcanizates," Rock Island Arsenal Laboratory, Report No. 63-2392, July 1963.
6. Rubber Manufacturers' Association Long-Term Shelf Aging Tests Data Report, March 1966.
7. "Effect of Shelf Aging on MIL-P-5516 O-Rings, Fourth Progress Report," Mare Island Naval Shipyard Rubber Laboratory, Report No. 92-15, January 1963.
8. "Storage Time Limitation Evaluation of O-Rings Conforming to MIL-P-5315 and Used in the Fuel System of S-2D (S2F-3) Aircraft," Pensacola Naval Air Station MEL Report P18-63, December 1963.
9. "Shelf Aging Project," Precision Rubber Products, Report to Rubber Manufacturers' Association, 1964.
10. "The Effect of Shelf Storage on the Properties of Silicone, Fluorosilicone, and Fluorocarbon Vulcanizates," Rock Island Arsenal Report to SAE, G-4, Elastic Seals Committee, Meeting No. 17, Washington, D. C., March 1966.
11. J. D. Lawyer and L. C. Fincher, "Long-Term Storage of MIL-P-5516 O-Rings," OCAMA, Tinker AFB, June 1966.
12. "Test of Average Elastomers," MOAMA, Brookley AFB, January 1966.

UNCLASSIFIED

## Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Monsanto Research Corporation 1515 Nicholas Road Dayton, Ohio 45407		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP N/A
3. REPORT TITLE LITERATURE SURVEY ON THE EFFECTS OF LONG-TERM SHELF AGING ON ELASTOMERIC MATERIALS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Summary Technical Report - November 1965 to November 1966		
5. AUTHOR(S) (Last name, first name, initial) Bellanca, Carmen L. Harris, Jay C.		
6. REPORT DATE August 1967	7a. TOTAL NO. OF PAGES 54	7b. NO. OF REFS 12
8a. CONTRACT OR GRANT NO. AF 33(615)-1484	8b. ORIGINATOR'S REPORT NUMBER(S)	
a. PROJECT NO. 7381		
c. Task 738102	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFML-TR-67-235	
d.		
10. AVAILABILITY/LIMITATION NOTICES This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAAE), Wright-Patterson Air Force Base, Ohio 45433		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Materials Applications Division Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433	
13. ABSTRACT  Literature was surveyed with regard to the effects of long-term storage on the properties of elastomeric compounds. Data showed that most elastomeric compounds aged well. Elongation at break appeared to be the property most commonly affected by age deterioration, although compression set and change in strain also are affected.		

DD FORM 1473  
1 JAN 64UNCLASSIFIED  
Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS		LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
O-Rings	Fluorosilicone						
Literature Survey	Fluorocarbon						
Elastomeric Compounds							
Long Term Aging	Physical Properties						
Accelerated Aging	Tensile Modulus						
Storage Life							
Elongation							
Age Deterioration							
Compression Set							
Vulcanizates							
Nitrile Elastomers							
Neoprene							
Butyl Rubber							
Silicone							

**INSTRUCTIONS**

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

UNCLASSIFIED

Security Classification